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Microstructure of Copolymers Containing Disperse Red 1 and Methyl Methacrylate

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ABSTRACT: Two series of copolymers containing disperse red 1 and methyl methacrylate have been synthesized: poly[4'-[[[2-(acryloyloxy)ethyl]ethyl]amino]-4-nitroazobenzene-co-methyl methacrylate] (poly(DR1A-co-MMA)) and poly[4'-[[[2-(methacryloyloxy)ethyl]ethyl]amino]-4-nitroazobenzene-co-methyl methacrylate] (poly(DR1M-co-MMA)). The sequence distribution of the two series of copolymers is calculated on the basis of the estimated reactivity ratio values and analyzed by ¹³C-NMR spectroscopy. Methyl methacrylate centered triad MMD, DMD, and MMM and disperse red 1 centered triad DDD fractions are derived from the α -methyl carbon of MMA and carbonyl carbon in poly(DR1A-co-MMA). Good agreement is found between the spectral deconvolution results and the calculated results. Polymer tacticity is analyzed with the main chain quaternary carbon and carbonyl carbon in poly(DR1M-co-MMA). No spectral sequence distribution information is available for this series.

Introduction

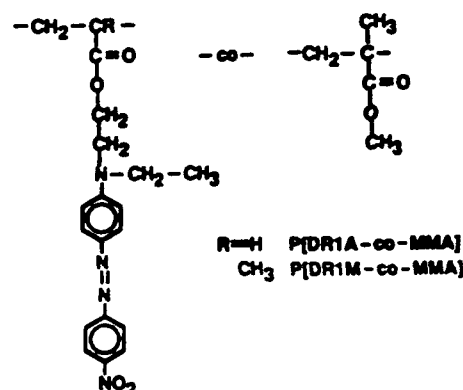
Azo polymers have attracted much attention as materials for optical applications.¹ The incorporation of chromophores with large second order hyperpolarizabilities into glassy polymers and the subsequent alignment (which is a poling process in strong electric fields) has been a promising technique in the search for useful materials for second order nonlinear optics.² In previous publications we have demonstrated that stable birefringence and dichroism can be optically induced in amorphous high T_g polymer films containing electron-donor-electron-acceptor substituted azobenzene groups.³⁻⁵ This phenomenon can be used to record optical information.

The poling process and optical storage process can take place in polymers with low azo concentrations. The usefulness of materials for such applications depends on the energy required to induce local variations of optical properties. In principle, a lower energy is required to write and erase information on azo polymers with low azo concentrations. There are two different ways to dilute the azo content in polymer materials. One is by copolymerization and is explored in this paper. The other is by mixing the azo polymers with other polymers to form polymer blends and is described in another paper.⁶

It is becoming increasingly clear that the macroscopic properties of bulk polymers are related to their molecular level microstructure. In the study of the molecular reorientation mechanism in azo polymers, the polymer tacticity and copolymer sequence distribution may play an important role. NMR spectroscopy has been proven to be the most powerful experimental tool for investigating the microstructure of various polymers including polyacrylates and polymethacrylates.^{7,8}

In the present paper we report the results obtained from the solution NMR investigation of two series of copolymers, poly[4'-[[[2-(acryloyloxy)ethyl]ethyl]amino]-4-nitroazobenzene-co-methyl methacrylate] (poly(DR1A-co-MMA)) and poly[4'-[[[2-(methacryloyloxy)ethyl]ethyl]amino]-4-nitroazobenzene-co-methyl methacrylate] (poly(DR1M-co-MMA)). The structures of the copolymer units are presented in Chart 1.

Chart 1



The two series of copolymers with similar repeating units and the same azo content are found to have different microstructures. The copolymer sequence distribution is first calculated on the basis of compositional data and then measured. Our preliminary optical tests on the two series of copolymers have shown that there are differences between the two copolymer series.

Experimental Procedures

Copolymer samples as well as homopolymers were synthesized by free-radical polymerization in toluene. Toluene (BDH, reagent) was dried by refluxing over sodium with a benzophenone indicator prior to use. The monomers DR1A and DR1M were prepared from disperse red 1 (DR1) (Aldrich) as previously reported.³ Methyl methacrylate (MMA) was purified by distillation before use. Solutions (0.5 M) of suitable mixtures of comonomers (DR1A and MMA or DR1M and MMA) were pipetted into glass ampules containing AIBN at a level of 10% by monomer weight. Nitrogen was bubbled through the solutions for 5 min. The ampule was then immersed in liquid N₂ and sealed, while the contents were frozen. The ampules were allowed to return to room temperature and then heated to 60 °C. The polymerization was allowed to proceed to high conversion at this temperature. Polymers were isolated from the reaction ampule after 2 days by precipitation into methanol followed by reprecipitation from tetrahydrofuran into methanol.

The molecular weights of the resulting polymers were estimated by gel permeation chromatography (GPC). A Waters Associates liquid chromatograph equipped with a Model 440 absorbance detector and a Model R401 differential refractometer was used. Peak molecular weights of ~4000 were obtained for the copol-

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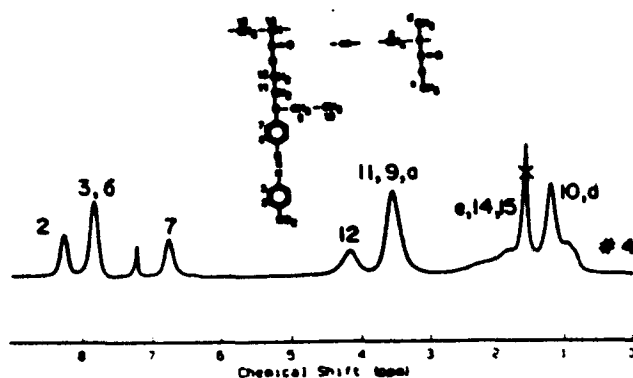
Figure 1. ^1H spectrum of poly(DR1A-co-MMA) 4.

Table 1. Details of Polymerization

copolymer	initial feed (DR1/MMA mol ratio)	composition (DR1/MMA mol ratio)	conversion (weight fraction)	glass transition temp ($^{\circ}\text{C}$)
Poly(DR1A-co-MMA)				
1	0.19	0.14	0.30	92
2	0.44	0.29	0.35	91
3	0.80	0.53	0.55	89
4	1.33	0.73	0.80	91
5	2.21	1.33	0.70	94
6	3.99	2.27	0.63	95
7	7.69	4.17	0.55	102
Poly(DR1M-co-MMA)				
8	0.09	0.06	0.54	114
9	0.20	0.06	0.61	112
10	0.36	0.11	0.58	110
11	0.60	0.29	0.53	120
12	0.81	0.38	0.58	120
13	1.28	0.71	0.50	120
14	2.32	1.79	0.47	119
15	5.59	4.45	0.41	122

ymers and homopolymers. The molecular weights of the polymers and copolymers were limited by the amount of initiator (10% weight) used in the polymerization reaction in order to obtain a better yield. However, when a lower amount of initiator (1% weight) was used, the molecular weight of the polymers was not higher. But the yields were very poor in this case.

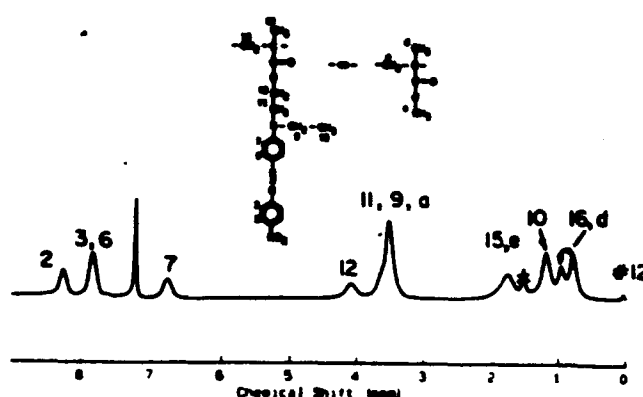
The glass transition temperatures of the copolymers were measured by differential scanning calorimetry. A Mettler TA 3000 thermal analysis system equipped with a TC10A TA processor and a DSC30 head was used. Heat flow vs temperature data were obtained at the second scan with a scanning rate of $20^{\circ}\text{C}/\text{min}$. Details on initial monomer ratios, glass transition temperatures, the identification number, and the composition of the product polymers are presented in Table 1.

The composition and the microstructure of the homopolymers and copolymers were analyzed on a Bruker AC-F 200 NMR spectrometer using standard pulse sequences for proton spectra. Carbon-13 NMR spectra were obtained on a Bruker AM-400 spectrometer and were collected for more than 10 h with gated decoupling and a 6-s delay between pulses. The solution samples for ^{13}C -NMR were prepared using 0.5 g of polymer in CDCl_3 with 10-mm sample tubes. All samples were run in deuteriochloroform solution.

Spectral deconvolution of the Fourier-transformed spectra was done with NMR286 from Softpulse Software, a program for the processing of NMR spectroscopy data on a personal computer. Lorentzian line shapes were used for all spectra.

Results and Discussion

Determination of Copolymer Compositions and Reactivity Ratios. The copolymer compositions are analyzed from proton NMR spectra. Figure 1 depicts the ^1H -NMR spectrum of poly(DR1A-co-MMA) (copolymer 4) as an example for this copolymer series. The ^1H -NMR spectrum of homopolymer PDR1A has been assigned in

Figure 2. ^1H spectrum of poly(DR1M-co-MMA) 12.

a previous publication.³ The assignments of the copolymer spectrum shown in Figure 1 are made by comparison with the spectra of the homopolymers. Similar ^1H -NMR spectra have been obtained for PDR1M and poly(DR1M-co-MMA) copolymer series. In Figure 2, the ^1H -NMR spectrum of poly(DR1M-co-MMA) (copolymer 11) is shown. The copolymer compositions can be readily obtained by the ratio of the integrated peak areas of the aromatic region and the aliphatic region. The results are listed in Table 1.

Reactivity ratios of the high conversion copolymerization can be estimated by the Kelen-Tudos (KT) high conversion formula, which is based on the simplest kinetic model of copolymerization, the terminal model.⁹ The calculated reactivity ratios for the two series of copolymers are

$$\text{poly(DR1A-co-MMA): } r_{\text{MMA}} = 1.29 \quad r_{\text{DR1A}} = 0.45$$

$$\text{poly(DR1M-co-MMA): } r_{\text{MMA}} = 4.00 \quad r_{\text{DR1M}} = 1.20$$

For both systems, MMA is more reactive than the DR1 monomer, but the results for poly(DR1M-co-MMA) are surprising. Normally, a methacrylate-methacrylate pair should generate a reactivity ratio product close to unity. Here the values suggest a tendency to form a block sequence for both comonomers. This is probably a result of approximations introduced by the method used and of the spread of the points in the KT graph. It is not within the scope of this paper to compare various copolymerization equations and their applicability to our system.

What follows is a test of the reliability of the reactivity ratio values obtained by the Kelen-Tudos method to predict the actual copolymer composition. The compositions are calculated from the copolymerization equation stepwise with a 10% conversion increment and then added up to the final conversion. The compositions calculated from the copolymerization equation are compared in Figure 3 with the experimental compositions derived from the NMR spectra. The vertical axis, f_{DR1} , is the copolymer composition expressed as the mole fraction of the disperse red 1 repeating units in the copolymer. The horizontal axis, F_{DR1} , is the feed monomer composition expressed as the mole fraction of disperse red 1 monomer in the monomer feed. The agreement between the calculated and experimental compositions is good for both series of copolymers, which means that the Kelen-Tudos formula can be reasonably used to estimate the reactivity ratios.

Carbon-13 NMR Sequence Analysis. Poly(DR1A-co-MMA). The reactivity ratios calculated via the Kelen-Tudos method could also be used to predict sequence distributions. Assuming the first order Markov model to be valid, the fractions of the methyl methacrylate centered

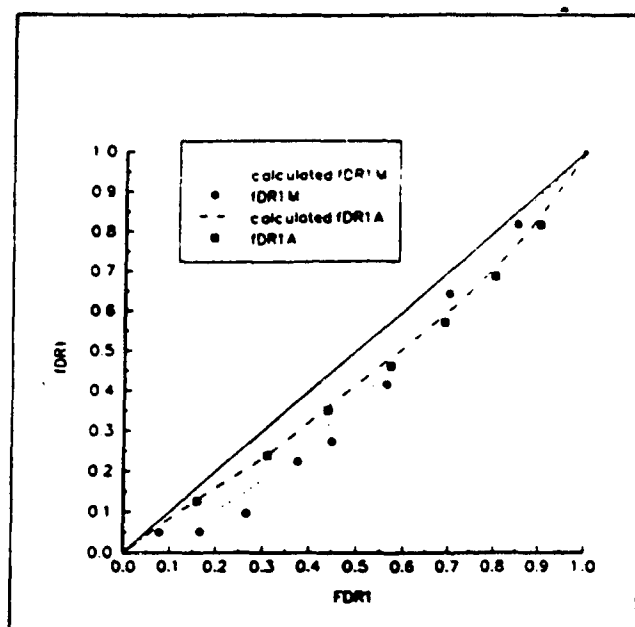


Figure 3. Polymer composition as a function of feed composition for the two series of copolymers.

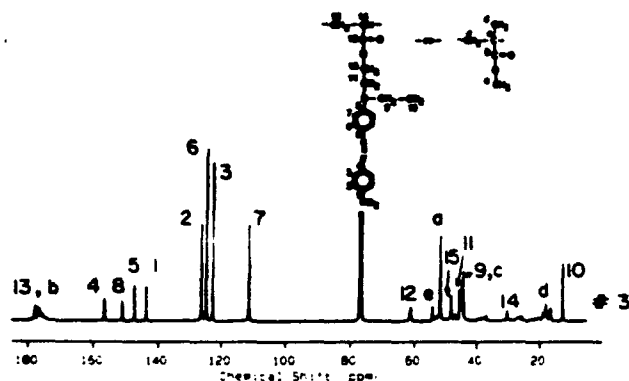


Figure 4. ^{13}C spectrum of poly(DR1A-co-MMA) 3.

triads (f_{MMM} , f_{DMM} , and f_{MDM}) and disperse red 1 centered triads (f_{DDD} , f_{DDM} , and f_{MDM}) can be calculated. Since the calculation is affected by changes in feed composition for the high conversion copolymerizations, cumulative triad distributions were calculated stepwise with a 10% conversion increment. The final results are obtained by summation of the triad fractions over the final conversion in copolymerization. The calculated sequence distributions of the copolymers are used as comparisons to the experimental results derived from ^{13}C -NMR spectra.

The proton decoupled ^{13}C -NMR spectrum of copolymer 3 is presented in Figure 4. The assignment of resonances to individual carbon atoms is made on the basis of J -modulated spectra of the copolymers and from the known assignments of PMMA as well as the published results of some azo polymers.^{7,10,11} The ^{13}C -NMR spectra of the series of copolymers are consistent with a regular head-to-tail arrangement of monomeric units. Within the limits of instrumental sensitivity, no signal corresponding to either head-to-tail or tail-to-tail linkage can be observed.

At first we consider the ^{13}C -NMR signals of the carbonyl carbons (C_{13} and C_b) of DR1A and MMA in the copolymer series for sequence analysis. The carbonyl signals in this series are depicted in Figure 5. In PDR1A, the carbonyl signal appears as a single broad peak around 174 ppm. The intensity of the signal at this position decreases as the concentration of DR1A decreases. On the other hand,

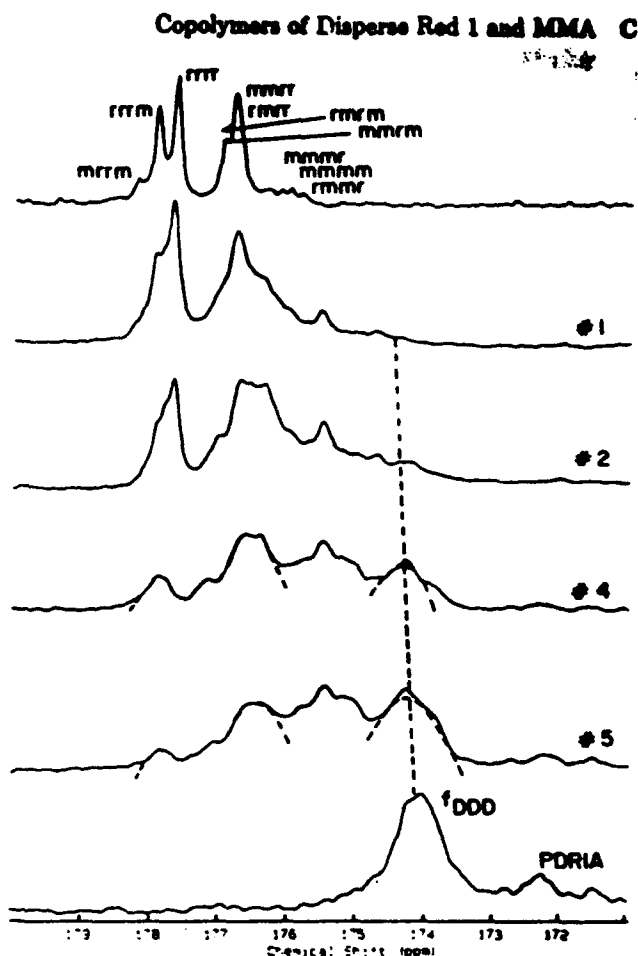


Figure 5. ^{13}C spectra of carbonyl carbons of PDR1A, PMMA, and poly(DR1A-co-MMA) 1, 2, 4, and 5.

PMMA homopolymer signals range from 176 to 179 ppm, showing at least six resonance lines. The peaks correspond to mrrm, rrrm, rrrr, rrmr + mrrm, rmrr + mrrr, and mmmm + mmmr + rmmr with increasing field according to Peat and Reynolds.²⁰ In the poly(DR1A-co-MMA) copolymer series, the resonance at 174 ppm is assigned to the azo group centered triad (DDD sequence). The resonances at 176–179 ppm are assigned to the methyl methacrylate centered triad (MMM sequence). Spectral patterns of the carbonyl carbons in this series of copolymers are very complicated. Spectral deconvolution results are scattered due to the complexity of the signals subjected to deconvolution. Only those resolvable peaks at 174 and 176–178 ppm were used for the calculation of the f_{DDD} and f_{MMM} sequences. The rest of the resonances which are the intermediate peaks between 174 and 176 ppm were not considered here because their assignments are not straightforward.

After curve fitting, the deconvoluted peak areas of 174 and 176–179 ppm are plotted as a function of composition. Figure 6 shows the experimental fractions of f_{DDO} and f_{MMM} for this series of copolymers. Calculated triads f_{DDO} and f_{MMM} are also plotted in Figure 6, showing that the assignment is probably correct and the correlation is fairly good.

Examination of the spectra also reveals that the α -methyl carbon (C_d) resonances from MMA are sensitive to sequence distribution. Figure 7 depicts the signals in the 15–22 ppm range for PMMA and copolymers 1, 4, and 6. The α -methyl carbon of PMMA has two main signals at 16.2 and 18.6 ppm, which can be assigned to rr and mr triads, respectively.¹⁰ In the copolymer series, resonances at the same chemical shifts are deconvoluted and added

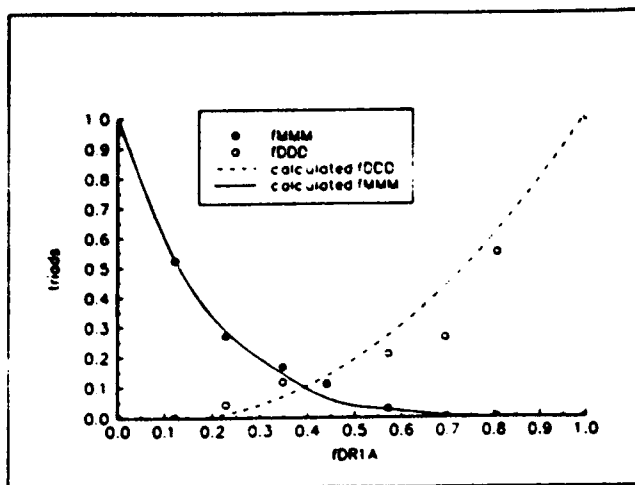


Figure 6. Calculated and experimental triad (DDD and MMM) fractions in poly(DR1A-co-MMA) obtained from the deconvolution of the carbonyl signals.

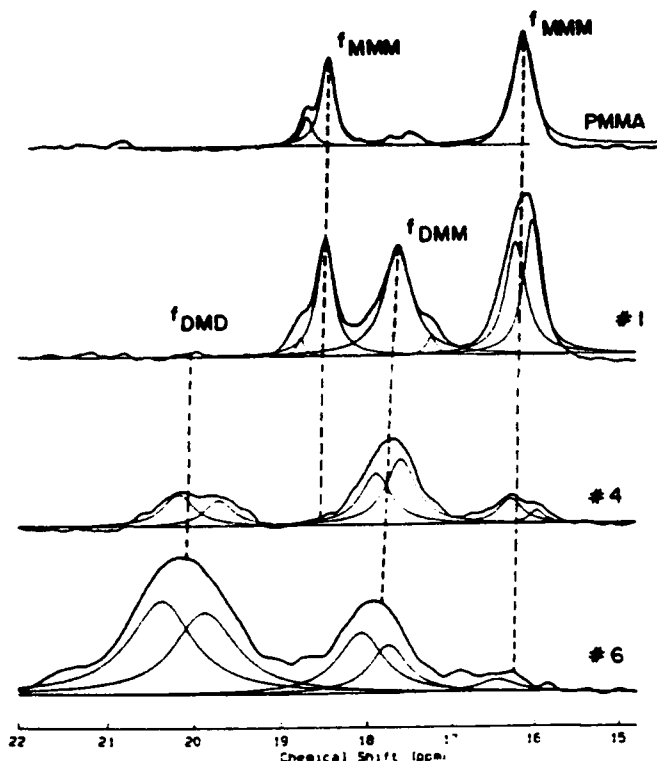


Figure 7. ^{13}C spectra of the α -methyl carbon (C_α) of PMMA and poly(DR1A-co-MMA) 1, 4, and 6.

up to generate the MMM triad sequence. There is no resonance from PDR1A in this area; therefore all the signals have to be assigned to MMA centered triads (f_{MMM} , f_{DMM} , f_{MMD}). As the MMA concentration decreases, a new broad signal at about 20 ppm labeled f_{DMD} increases. This peak reaches maximum intensity at the highest composition of DR1A in the copolymer and therefore is assigned to the DMD sequence. The signal marked as f_{DMM} is an intermediate peak for copolymers at about 18 ppm.

The results of the calculated and experimental sequence distributions are presented in Figure 8, where the dashed, dotted, and solid lines represent calculated f_{MMD} , f_{DMD} , and f_{MMM} sequences, respectively. The results show a good agreement between the deconvoluted and calculated data.

In this series of copolymers, we have assigned DDD triads and MMA centered triads (MMD, DMD, MMM) in the ^{13}C -NMR spectra. Some of the calculations based on the

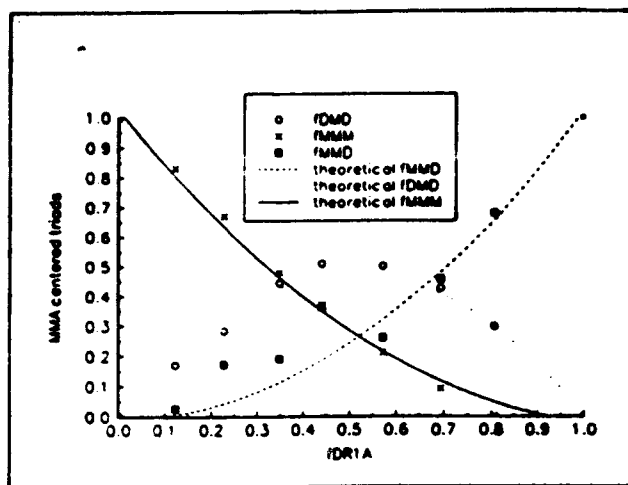


Figure 8. Calculated and experimental MMA centered triad fractions obtained from the α -methyl carbon (C_α) signals.

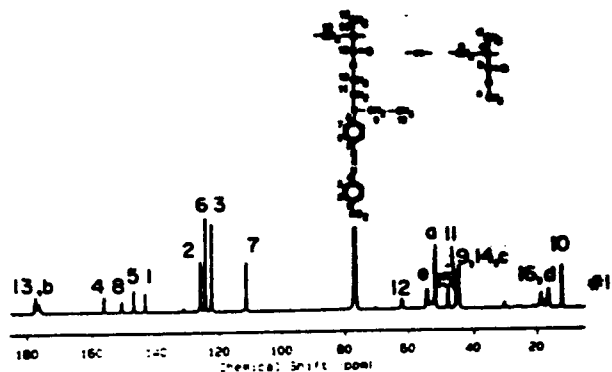


Figure 9. ^{13}C spectrum of poly(DR1M-co-MMA) 11.

first order Markov model have been confirmed by NMR spectroscopy. Data on DR1A centered triads other than f_{DDD} are not available in the spectra. However, there is good agreement between the ^{13}C -NMR results and the calculated results and it seems reasonable to assume that the first order Markov model for sequence distribution is valid in the poly(DR1A-co-MMA) series.

Poly(DR1M-co-MMA). The proton-decoupled ^{13}C -NMR spectrum of copolymer 11 is presented in Figure 9, together with the assignments.

In the PMMA spectrum, carbon C_α exhibits three peaks. As depicted in Figure 10, the peaks are assigned to isotactic (mm), syndiotactic (rr), and heterotactic (mr) triads.¹⁰ In the copolymer series, C_{14} and C_α carbons resonate together. However, the resonance of the mm triad is superimposed by the C_α and C_{11} signals from PDR1M. The signals at 44.6 and 44.9 ppm were deconvoluted. The probability of forming a meso diad (σ) can be calculated from the ratio of the peak areas (mr/rr) as follows

$$\frac{\text{mr}(44.9 \text{ ppm})}{\text{rr}(44.6 \text{ ppm})} = \frac{2\sigma(1-\sigma)}{(1-\sigma)^2}$$

σ is plotted as a function of copolymer composition in Figure 11. σ increases linearly as the DR1M concentration in the copolymer increases. In this case, we are dealing with meso diads from all sequences including DD, MM, and MD. The average syndiotactic fraction decreases with increasing azo content in the copolymer series which means that the azo copolymers are less syndiotactic than PMMA. This is probably because that, in DR1M, there are two methylene units between the azo group and the main chain which allow more flexibility during the free-radical po-

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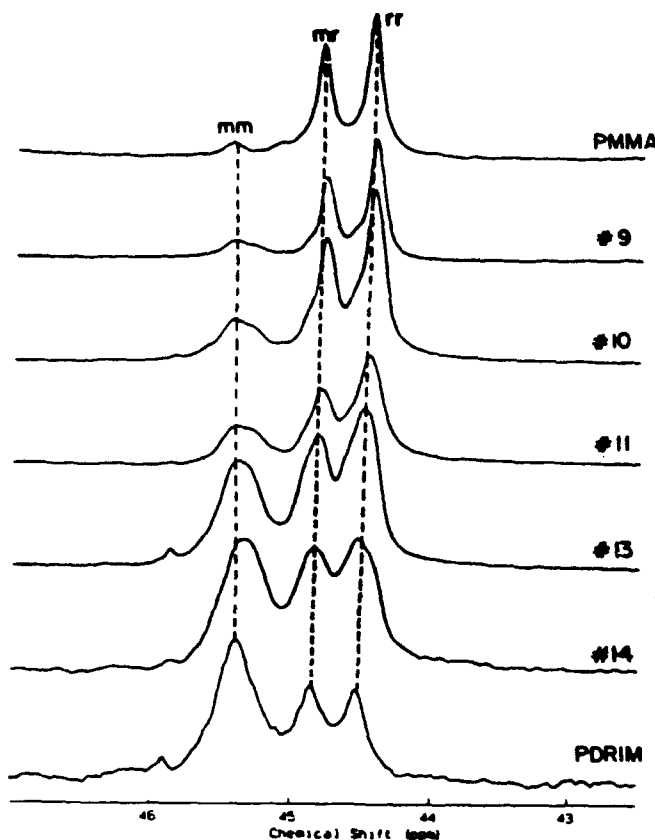


Figure 10. 43–47 ppm region of the ^{13}C spectra of PMMA, PDR1M, and poly(DR1M-co-MMA) 9–11, 13, and 14.

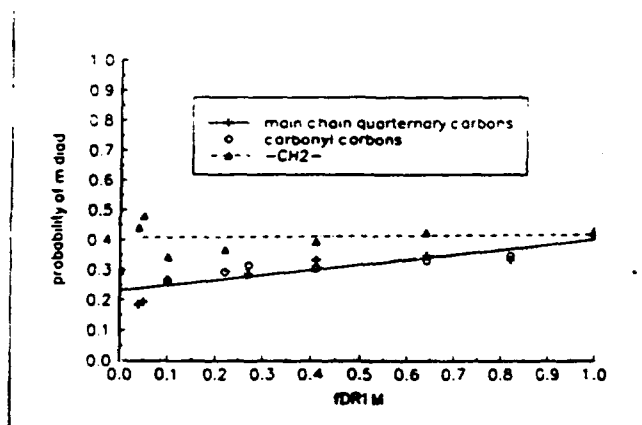


Figure 11. Probability of meso diad formation calculated from the main chain quaternary carbon and carbonyl carbon signals.

lymerization. The σ value for PDR1M is 0.4, which is very close to a random configuration distribution.

The carbonyl carbon signal of PDR1M appears split by pentad tacticity. At least seven separate lines can be resolved from the signal. According to Altomare et al.,¹¹ the resonances of the carbonyl signals can be tentatively assigned to mrrm, rrrm, rrrr, mmrm, rmmr, rrrr, mmrr, mmm, mmmr, and rmmr pentads, as shown in Figure 12. This proposed assignment is similar with that reported for poly(methyl methacrylate).¹⁰

The probability of forming a meso diad (σ) can also be calculated from the carbonyl signals in the copolymer series. The results are shown in Figure 11 together with those calculated from the main chain quaternary carbons.

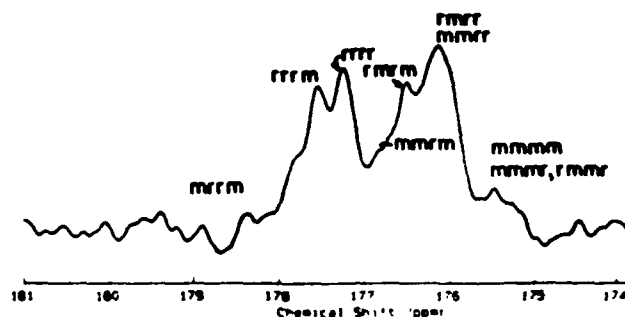


Figure 12. ^{13}C spectrum of the PDR1M carbonyl carbon.

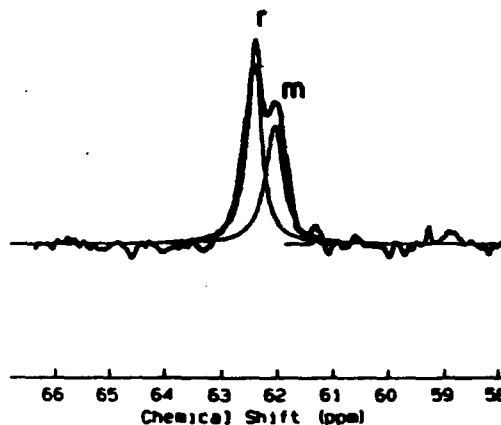


Figure 13. ^{13}C spectrum of the C_{12} of PDR1M.

Good agreement is found for the tacticity analysis from the two signals. Because of overlapping between the carbonyl signals from MMA and DR1M, this is the only information that can be obtained from this spectral region.

The signal corresponding to the C_{12} carbon atom of PDR1M at about 62 ppm is split into two resonance peaks (Figure 13). Assuming only configurational contributions, the peaks at about 62.0 and 62.5 ppm are assigned to r and m diads, respectively, as shown in Figure 13. The C_{12} signals from the copolymers show a similar split. The probability of forming m diad (σ) has been calculated from these signals and is presented in Figure 11. The data are rather scattered because the two signals are not very well separated in this case. PMMA does not resonate in this region; therefore these signals represent only the tacticity of DR1M units. Thus the probability of forming a meso diad does not depend on copolymer composition, as expected. σ is about 0.4, which is the same value as found from the other signals previously analyzed.

In this series of copolymers, we have been only able to obtain information on main chain tacticity from the ^{13}C -NMR spectra. Sequence analysis is not possible due to signal overlapping.

Conclusions

Two series of copolymers containing disperse red 1 and methyl methacrylate have been synthesized, and their microstructures have been analyzed. The reliability of the data for the poly(DR1A-co-MMA) series was proven by ^{13}C -NMR spectroscopy. However, the experimental data on the sequence distribution of the poly(DR1M-co-MMA) series is not available from ^{13}C -NMR spectroscopy. If the calculated sequences are true, the results will be of practical interest. In optical storage processes DR1 acts as the optically active group, while MMA is inert to light. The two copolymer series seem to have a fairly different

sequence distribution to allow us to study the effect of the next neighbor in this process.

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